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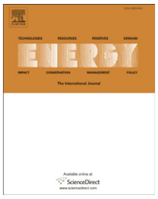

Effect of temperature and dolomite on tar formation during gasification of torrefied biomass in a pressurized fluidized bed

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ABSTRACT

This work investigates the effect of temperature and bed material on the yields and composition of gas and tar produced from gasification of two types of biomass feedstock previously torrefied at 275 °C. Special attention was devoted to the evolution of tar composition under the different experimental conditions. Experiments were conducted in a fluidized bed reactor using two different types of bed material (sand and dolomite) under a constant pressure of 0.5 MPa and at two temperature levels (750 and 850 °C). Tar destruction reactions promoted by the catalyst (dolomite) enhanced the production of some of the gas components (H_2, CO_2, CO and CH_4) whereas C_2 hydrocarbons decreased, this effect being slightly more relevant at 850 °C. Comparable trends were observed with increasing temperature, which had a positive effect on cracking reactions and tar destruction. For both feedstocks, the increase in temperature resulted in (i) higher gas yields, and (ii) enhanced char gasification rate. On the other hand the evolution of tar yield and composition revealed a possible competition between two tar reaction pathways during gasification, (i) tar polymerization, and (ii) de-alkylation, dehydration and cracking of tars, depending on the experimental conditions and feedstock used.

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1. Introduction

Biomass is a renewable energy source that can be converted into other marketable energy carriers such as electricity (via CHP (combined heat and power)), liquid fuels (BTL (biomass-to-liquids route)) and gaseous fuels (such as SNG (synthetic natural gas)). Gasification is considered the core technology in the thermochemical route of biomass valorization to heat and power, synthetic fuels and chemicals, as it converts biomass efficiently and with high conversion rates. Tar formation is one of the major challenges in current thermal gasification technologies, and particularly during biomass gasification. Tar is a condensable organic product compounded mainly by olefins, phenolics, mono- and poly-nuclear aromatics, heterocyclic aldehydes and alkyl derivatives of aromatics [1]. Tars formed during biomass gasification may condense and tend to polymerize into more complex structures, which represent a serious drawback for the use of producer gas, both for CHP and synthesis of biofuels or other chemicals. Condensed tars, particularly when mixed with char and fly ash particles, cause clogging and fouling in downstream boilers, gas cleaning systems and catalytic reactors, and deactivate the downstream catalysts. Additionally, condensed liquid tars and polymerized solid particles can cause rapid mechanical damages due to erosion in gas-turbine blades. These technical issues related to tar formation typically lead to high operation and maintenance costs in commercial-scale facilities, associated to unscheduled plant shutdowns and equipment maintenance and repair. Removal of tars from the gas stream after gasification, although necessary to achieve the gas purity required by its downstream processing, increases operation costs and reduces the thermal efficiency of the gasification unit, since tars retain a significant fraction of the energy of the biomass fuel. In this context, further integration of biomass gasification into commercial-scale biofuels production systems and high-efficiency CHP facilities relies on the in-situ decomposition of tars into lighter syngas components.

The extensive research available in literature related to tar formation has mainly focused on experimental characterization of tars produced from biomass pyrolysis and gasification under various operating conditions [2–9]. However, a more detailed understanding of the interdependence among the kinetics of tar decomposition and tar polymerization, the process conditions typically present in commercial-scale gasification technologies, and

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the performance of tar-decomposing catalysts is still needed to optimize the in-situ conversion of tars into lighter gas components. Several process parameters have been identified to influence the formation of tars during biomass pyrolysis and gasification: biomass composition and particle size, bed material, temperature, pressure, and composition and flow rate of the gasification agent. The selection of these parameters, particularly the operating conditions, also depends on the type of gasifier under consideration.

The dependence of tar formation and composition on temperature has been extensively investigated. Primary tars are formed during the early stages of biomass pyrolysis inside the particles at temperatures between 200 and 300 °C, being the heating rate of the biomass particles a key parameter to influence the composition of the primary tar compounds that are formed [1]. Primary tars then evolve to secondary and tertiary tar compounds as temperature increases. Experimental investigations above 750 °C have shown that as temperature increases the total tar content gradually decreases [2–7], due to tar cracking and steam reforming, and that the formation of tertiary aromatic tars, mainly naphthalenes and fluorenes, from secondary tars is enhanced [1,2,4,5,7–9].

Experimental investigations on biomass gasification have also shown that the choice of gasification agent plays an important role on tar content and its composition. In practice, air (both atmospheric and oxygen-enriched) and steam have been used as oxidants for gasification. Therefore two separate process parameters have been typically reported in the literature to describe the overall biomass gasification process: (1) the ER (equivalence ratio) defined as the moles of oxygen available for gasification divided by the total moles of oxygen required for stoichiometric biomass combustion [9] and (2) the S/B ratio (steam to biomass ratio) defined as the total mass of steam divided by the total dry mass of biomass during gasification [4]. In the particular case of steam gasification, reported experimental results have shown that increasing the S/B ratio reduces the tar yield due to enhanced steam reforming reactions [4,6,10,11], although the effect on tar composition depends on the operational temperature. At sufficiently high temperature, above 800 °C, all tar species decrease with the S/B ratio, but below 750 °C the increase of S/B ratio diminishes secondary tars but increases light aromatic tertiary tars [4]. A decrease of tar yield with increasing ER has also been observed experimentally [9,12], showing a tar reduction of about 50 wt.% when ER was increased from 0.2 to 0.45 [9].

The type of feedstock and thermal pretreatment of biomass, like torrefaction, also have a significant influence on tar yields from gasification. Torrefaction is a thermochemical process that subjects the feedstock to temperatures between 200 and 320 °C in an inert atmosphere improving some characteristics of the product such as higher energy density, lower moisture content, higher hydrophobicity and higher reactivity during combustion and gasification [13–15]. Torrefied biomass has also been reported to reduce tar formation [16,17], as a consequence of the partial removal of oxygenated constituents of biomass [18] and volatiles during the torrefaction process.

The use of catalysts and additives to reduce tars formation in biomass gasification has also been extensively investigated [1,19–28]. Three main groups of catalysts being reported to be successful in removing tars from the producer gas [29]: (1) natural catalysts such as dolomite and olivine; (2) alkali-based catalysts such as Li, Na, K, Rb, Cs and Fr and (3) metal-based catalyst such as nickel catalysts. In the present study dolomite was used as catalyst. The use of dolomite for biomass gasification in fluidized bed is attractive since it is a cheap material and exhibits proven catalytic activity and effectiveness to reduce tars both in laboratory-scale gasifiers and pilot plants [25]. Dolomite is more effective than olivine as catalyst although is less resistant against attrition [20,22] and generates more particulates in the product gas [20]. Calcined dolomite has shown even better efficiency for increasing hydrogen content as compared to raw dolomite and olivine [30]. Several experimental works on the gasification of woody biomass in fluidized bed have reported the benefits of using dolomite on tar depletion [9,31,32]. Narvaez et al. [9] used calcined dolomite (3 wt.%) mixed with the processed biomass and found that the tar content decreased from 10 to 4 g/Nm^3. This reduction is in agreement with data reported by Miccio et al. [32] who observed a tar reduction up to 50% by using this catalyst as bed material. A former study by Gil et al. [31] concluded that with a 15–30 wt.% of calcined dolomite in bed, tar contents below 1 g/Nm^3 could be obtained.

This work investigates the effect of temperature and bed material on the product yields and composition of gas and tar produced from gasification of two types of biomass feedstock (GROT-ST and VW-ST) previously torrefied at 275 °C. Special attention was devoted to the evolution of tar composition under the different experimental conditions. Experiments were conducted in a fluidized bed reactor using two different types of bed material (sand and dolomite) under a constant pressure of 0.5 MPa and at two temperature levels (750 and 850 °C). This study continues a previous work where the effect of torrefaction level and pressure were studied at 850 °C. The obtained results, showing higher tar content, together with higher levels of aromaticity, as pressure increased led to a more detailed study on tar evolution combining torrefaction and the presence of catalyst, in order to reduce the amount of tar in the gas. The results here presented will contribute to the understanding of the interdependence between the kinetics of tar decomposition and tar polymerization when dolomite is used as bed material under typical commercial-scale gasification conditions.

2. Experimental

2.1. Materials

2.1.1. Biomass feedstock characterization and preparation

Norwegian spruce and Norwegian forest residues (mainly tops and branches), torrefied at 275 °C, hereby referred as VW-ST and GROT-ST respectively, were used as feedstock. Detailed information on the torrefaction experimental setup and operating conditions during torrefaction of the biomass feedstock has been described elsewhere [33]. Both feedstocks were sieved to a particle size range of 250–500 μm. The proximate and ultimate analyses were carried out using a LECO TGA (Thermogravimetric analyzer 701) and a LECO TruSpec CHN–S–O analyzer respectively. The proximate analyses of all samples were conducted following the ASTM D7582

Table 1
Main characteristics of feedstocks.

		VW-ST	GROT-ST
Ultimate analysis[a] [wt.%]	C	52.72 ± 0.29	56.84 ± 0.08
	H	5.88 ± 0.11	5.51 ± 0.10
	O	40.86 ± 0.40	34.29 ± 0.20
	N	0.06 ± 0.02	0.61 ± 0.02
	S	0.03 ± 0.002	0.06 ± 0.004
	F	<0.0015	0.051 ± 0.0011
	Cl	0.0021 ± 0.0003	0.0131 ± 0.0007
	P	0.0021 ± 0.0005	0.0216 ± 0.0028
Proximate analysis[a] [wt.%]	Moisture	3.79 ± 0.01	4.17 ± 0.01
	Volatiles	72.34 ± 0.06	61.63 ± 0.11
	Fixed carbon	23.41 ± 0.05	31.47 ± 0.11
	Ash	0.46 ± 0.01	2.73 ± 0.02
LHV [MJ/kg][a]		16.12 ± 0.03	18.29 ± 0.029

[a] "As received" basis.

standard test method for moisture, volatile matter, and fixed carbon determination. The results together with the LHVs (lower heating values) are included in Table 1. The determination of the heating value of the samples was performed in an isoperibolic LECO Automatic calorimetric bomb (AC600), according to the ASTM D5865-07 standard test method.

2.1.2. *Bed material*

Sand and dolomite sieved to a particle size of 150–200 μm, were used as bed materials. Dolomite was kindly provided by MINELCO GmbH; its composition was as follows: CaO 30.2%, MgO 21.6%, Al_2O_3 0.06%, SiO2 0.1%, Fe_2O_3 0.03% and carbonate (as CO_2) 44.4%. Previous to its use as bed material, dolomite was calcined at 900 °C for 4 h. Note that both bed materials were fully replaced for each experiment.

2.2. *Fluidized bed gasifier*

The experimental setup and procedure have been described elsewhere [33]. Briefly, the fluidized bed reactor consists in a 404-mm-long (23.8 mm internal diameter) Hastelloy C column, capable of operating at pressures of up to 20 bar and temperatures of up to 900 °C (PID ENG&Tech, Spain). The reactor was externally heated using an electrical furnace. Bed temperature and freeboard temperatures were measured and controlled by two thermocouples placed inside the bed and freeboard respectively. The solid fuel was continuously fed into the bed by means of a screw feeder, at feed rates from 0.2 to 5 g/min. Water flow was pumped into the steam generator using a GILSON HPLC pump (0–5 mL/min range) before it was injected in the reactor. Notice that the experimental rig was equipped with a complete control system including, flow control, feeding system control, pressure control, together with several temperature measurement points, temperature control inside the fluidized bed and freeboard.

The volatiles released during the gasification process flowed across the bed and freeboard and then passed through a cyclone and hot filter to remove any particulate matter. After that, the gas was cooled in a condenser (5 °C) and an ice-salt tar trap (−10 °C). Additionally, stainless steel mesh was packed in the outlet arm of the trap to ensure efficient trapping of the condensed material in the form of aerosol droplets. The gasification-product gas composition and flow rate were measured by means of an online micro GC (Agilent 490) and a Bronkhorst High-Tech flow meter, respectively.

2.2.1. *Experimental procedure*

The required amount of feedstock was placed in the hopper, and the solid mixing and feeding screws were set to the desired feed rate. The reactor was filled with 50 g of sand/dolomite (particle size 150–200 μm), fluidized on a stream of N_2 (Praxair, Inc.) during the heating period up to the experiment temperature. During the heating period nitrogen stream from the reactor was vented, and the online micro GC (gas chromatograph) was calibrated using a gas calibration mixture. Once the desired temperature was reached, the fluidization gas flow was switched from N_2 to O_2 (Praxair, Inc.) and the system was pressurized to the experimental final conditions. The only N_2 gas entry in the system corresponded to the stream (50 mL/min) used for purging/pressurizing the biomass hopper. As soon as the system was stable, the solid and water feeds were switched on. A constant gas composition was reached after about 5 min of starting the feeding. These are the gas compositions reported in this study. The experiment length was about 60 min for all the performed tests.

Tars were recovered by washing the tar trap with a mixture of $CHCl_3$:MeOH (4:1 vol:vol). The solvent was removed by rotavap and then by purging with N_2 until the tar was completely dried. The remaining unconverted particles in the bed, filter and cyclone were collected and weighted after the completion of the test. During the experiments performed using dolomite as bed material, a slightly larger amount of solids was recovered in the filter, probably due to attrition of dolomite. However the degree of attrition was not considered relevant and, since the bed material was fully replaced for each experiment, this issue has not been studied in further detail.

Gasification was performed under O_2/steam atmosphere at 0.5 MPa, with an ER (equivalence ratio) around 0.23 and a steam/biomass ratio of about 1.6. The operation flows provided a fluidizing gas velocity five to six times the minimum fluidization velocity (U_{mf}), corresponding to gas residence times in the reactor of 2.3–2.6 s. Mass balances were calculated taking into account the mass of gases produced (gas balance) and the weight of tar and unconverted solid particles. Adequate global and elemental (C, H, O) mass balance closures ($\geq$95%) were obtained for all the conducted experiments. It should be noted that all the experiments were performed in duplicate.

2.3. *Gas and tar analysis*

An online micro GC (Agilent 490) was used to quantify the concentration of the major gas components produced during the experiments. The chromatograph configuration included three different channels: Channel 1, equipped with a 10 m MS5A (Molecular Sieve 5A), running on argon as carrier gas for the analysis of permanent gases other than carbon dioxide (H_2, O_2, N_2, CO and CH_4). Channel 2 was equipped with a 10 m PoraPlotQ and used helium as carried gas, allowing the separation of CO_2 and saturated and unsaturated C_1 to C_3 hydrocarbons. The C_3 to C_5 hydrocarbons were analyzed on the third channel (also using helium as carrier gas) with a 10 m Al_2O_3 column. Detection was carried out by means of μTCD (micro-machined thermal conductivity detectors) included in each channel.

Analysis of PAHs in the tars was performed using a Hewlett Packard 6850 GC–FID (gas chromatograph with a flame ionization detector) and an automatic sampler (7683B). A high-temperature capillary column (DB-5 phase, 15 m length, 0.32 mm i.d., 0.1 μm film thickness) was used for the analysis. Carrier gas was He at a flow rate of 1 mL/min. The injector and detector temperatures were 275 °C and 325 °C, respectively, while the oven temperature program started at 40 °C (held for 2 min) with a posterior ramp of 10 °C/min to 280 °C, and a ramp of 15 °C/min to 320 °C, held at 320 °C for 2 min. The sample was dissolved in $CHCl_3$ and 1 μL of the solution was injected, with a split ratio of 100:1. One standard solution (EPA 610 PAH Mix) was used for peak identification and area calibration. All the results were normalized to grams of tar per gram of dry biomass. To check the repeatability of the results three separate analyses were performed from each sample.

An Agilent Technologies 1100 Series HPLC system was used to perform the size exclusion analysis of the obtained tars. Three 300 mm long, 7.5 mm i.d. polystyrene/polydivinylbenzene-packed columns (PL Gel 10^4 Å 5 μm, PL Gel 500 Å 5 μm and PL Gel 50 Å 5 μm) were used (Polymer Laboratories, Church Stretton, UK). The system was operated at 80 °C and a flow rate of 0.5 mL/min. NMP (N-Methyl 2-pyrrolidinone) was used as the mobile phase. Detection was carried out using a diode array UV-absorbance detector. As NMP is opaque at 254 nm, detection of standard compounds and samples was performed at 270, 300, 350 and 370 nm, where NMP is partially transparent. The results obtained at 300 nm are considered representative of the main trends observed at all wavelengths; only those results will be shown and discussed. System calibration was carried out using two sets of standards, PS standards calibration is applied to the 30–52 min time range, while PAH (polycyclic aromatic hydrocarbon) compounds calibration is used in the 52–62 min region [34–36].

The calibration used to convert elution time to mass estimates was as follows:

Elution time	Calibration equation	Basis
<27.5 min	>200,000 u average mass (Mn)	
27.5–47.5 min	log (MM) = 8.6855–0.1232* (time)	Polystyrene (PS)
47.5–60.0 min	log (MM) = 6.0797–0.0682* (time)	PS + PAH std's
>60.0 min	Approximately 100 u	PAH std's

The structural features of the tar compounds were analyzed using FT-IR (Fourier Transform Infrared) spectroscopy, performed in a Bruker Vertex 70 spectrometer equipped with Platinum diamond ATR unit. Tar spectra were collected at room temperature in the range 400–4000 cm^{-1} by co-addition of 32 scans at a nominal resolution of 4 cm^{-1}, taking the spectrum of the empty cell at ambient conditions as the background.

3. Results and discussion

This section describes the results of the gasification experiments conducted on the torrefied biomasses. The gasification was performed under O_2/steam atmosphere, two different temperatures (750 and 850 °C) and two bed materials (sand and dolomite). Experimental conditions and product yields are listed in Table 2 and Table 3 respectively. Product yields were calculated as the percentage of mass of compound per mass of dry biomass. As a consequence of using this basis, total yields (sum of gas, tar and char yields) in excess of 100% are possible, since during the gasification reactions the products incorporate oxygen and hydrogen from the gasification agents (O_2 and steam).

3.1. Product yields

Table 3 presents the results obtained in terms of variation of gas, tar and char yields during the experiments under different conditions. The data show a clear effect of bed material on product yields, with higher gas and char yields and lower tar yield when dolomite is used as bed material instead of sand, for the two biomasses and temperatures studied. The use of dolomite instead of sand increased the gas yield for both types of biomass (around 14%) when gasification was performed at 750 °C, (comparing experiments 1–2 and 3–4) whereas the gas yield increase was less important (around 7% for VW-ST and about 2% for GROT-ST) at higher gasification temperature (850 °C) (experiments 5–6 and 7–8). Additionally, the effect of feedstock on the gas yield with increasing temperature presented some differences when using sand or dolomite as bed materials. When gasifying with sand, the increase of gas yield with temperature for GROT-ST (exp. 3–7) was higher (around 18%) than the increase of 13% obtained for VW-ST (exp. 1–5). The gas yield increase was similar for both biomasses when using dolomite as bed material (comparing experiments 2–6 and 4–8).

As it is shown in Table 3, at a gasification temperature of 750 °C the tar yield decreased when sand was replaced with dolomite as bed material by 51% and 14% for VW-ST (exp. 1–2) and GROT-ST (exp. 3–4), respectively. The effect of dolomite on tar depletion was even more significant at 850 °C, with tar yields decreasing by 81% and 63% for VW-ST (exp. 5–6) and GROT-ST (exp. 7–8), respectively.

Replacing sand by dolomite also increased the char yield, although the effect was different for the two types of biomass feedstock. The increase of char yield by using dolomite for gasification of GROT-ST did not show a significant dependence with temperature, the increase being 34% at 750 °C (exp. 3–4) and 38% at 850 °C (exp. 7–8). However, during gasification of VW-ST, the effect of dolomite in increasing the char yield was small at 750 °C (11% increase, exp. 1–2) but quite significant at 850 °C, with an increase of 90% (exp. 5–6).

These results confirm the catalytic effect of dolomite as bed material to convert tar in-situ and therefore reduce the tar yield. This can be explained by the fact that dolomite enhanced the formation of the other two reaction products, namely gas and char (via tertiary aromatics) through de-alkylation reactions. As previously stated, the catalytic effect of dolomite to reduce tar yield was more noticeable at higher temperature. Additionally, comparing the results between sand and dolomite, the gas yield increase was lower at 850 °C (exp. 5–6 and 7–8) in comparison to 750 °C (exp. 1–2 and 3–4), for both torrefied materials. These results, together with the evolution of char yield, indicate an increased effect of dolomite to enhance polymerization reactions to form char from de-alkylized tertiary aromatics. Data also indicate that temperature enhanced char gasification reactions. This effect, particularly relevant in this temperature range for the steam gasification reaction, led to higher gas and lower char yields [37,38].

3.2. Gas composition

Table 4 shows the dry and N_2 free average composition (vol.%) of the gas product measured during the gasification experiments. The obtained gas presented a quite stable composition along the experiments (about 60 min) in all the cases. Notice, that the data are presented as N_2 free, nonetheless the actual value of N_2 percentages in the produced gas was typically lower than 2% (as the only N_2 entry in the system was the flow to purge/pressurize the biomass hopper). The main gas components were H_2, CO_2, CO and CH_4, whereas C_2H_6, C_2H_4 and C_3H_8 appeared in lower concentrations. The yields of the main gas species (g per 100 g of dry biomass) are shown in Fig. 1.

The results in Fig. 1 and Table 4 show an increase in the total H_2 yields and dry concentration both with increasing temperature (comparing exp. 1–5, 2–6, 3–7 and 4–8) and when sand is replaced with dolomite as bed material (exp. 1–2, 3–4, 5–6 and 7–8) for both types of biomass. The hydrogen yields (see Fig. 1) obtained at 750 °C were in the order of 3.6 and 3.4% for VW-ST and GROT-ST, respectively, when sand was used as bed material, and 4.6–4.5% with dolomite. At 850 °C the hydrogen yield was 4.8% and 5.1% for VW-ST and GROT-ST, respectively, with sand as bed material and 5.5% with dolomite for both biomasses. Several authors [3,4,7,9,29,37,39,40] have also found that increasing the temperature results in a higher hydrogen content in the producer gas, which could be explained by the increase of the rates of steam gasification and steam reforming of hydrocarbons, leading to larger production of hydrogen. The effect of dolomite in increasing the H_2 production has also been reported previously [20,25], and was explained by the catalytic effect of dolomite towards the de-alkylation of tars as well as the steam reforming of hydrocarbons and the CO water gas shift reaction.

Fig. 1 also shows, for both biomasses, an increase in the methane yield with increasing temperature and when using dolomite. The methane yield for GROT-ST gasification using sand and dolomite increased from 6.0 and 7.2% at 750 °C, respectively, to 8.5 and 8.7% at 850 °C, under the same pressure and gasification agent conditions. The experimental results also showed that the effect of dolomite in increasing CH_4 production was more significant for VW-ST than GROT-ST. This trend can be explained since both temperature and presence of dolomite favour the de-alkylation of tertiary aromatic tars and cracking of aliphatic hydrocarbons towards methane as

Table 2
Main experimental conditions.

Run	1	2	3	4	5	6	7	8
Feedstock	VW-ST	VW-ST	GROT-ST	GROT-ST	VW-ST	VW-ST	GROT-ST	GROT-ST
Temperature (°C)	750 ± 2	750 ± 3	750 ± 3	750 ± 2	850 ± 4	850 ± 3	850 ± 4	850 ± 5
Pressure (MPa)	0.5 ± 0.01	0.5 ± 0.01	0.5 ± 0.01	0.5 ± 0.01	0.5 ± 0.01	0.5 ± 0.01	0.5 ± 0.01	0.5 ± 0.01
Bed material	Sand	Dolomite	Sand	Dolomite	Sand	Dolomite	Sand	Dolomite
Fuel[a] input (g/min)	1.47	1.49	1.37	1.34	1.44	1.45	1.41	1.32
O_2 input (NmL/min)	370	380	390	390	380	380	390	390
N_2 input (NmL/min)	50	50	50	50	50	50	50	50
H_2O (g/min)	2.2	2.2	2.1	2.1	2.2	2.2	2.1	2.1
ER	0.23	0.23	0.23	0.24	0.24	0.24	0.23	0.24
g H_2O/g dry biomass	1.6	1.6	1.6	1.7	1.6	1.6	1.6	1.7
t_r reactor[b] (s)	2.6	2.4	2.6	2.5	2.3	2.3	2.4	2.4
U_f/U_{mf}	5.6	6.0	5.5	5.8	6.2	6.3	6.0	6.1
Mass balance (% wt.)	97.0	98.1	96.1	97.5	98.8	99.1	95.8	96.7

[a] As received.
[b] Bed conditions.

final product. This effect surpassed the equilibrium of the methanation reaction, which shifts towards H_2 and CO when temperature increases due to its exothermic character. Table 4 shows that the dry CH_4 concentration obtained from gasification of GROT-ST increased also both with temperature (exp. 3–7 and 4–8) – in agreement with previous results on gasification of wood at similar pressure and temperature conditions [3,7] – and when using dolomite (exp. 3–4 and 7–8). However, the dry concentration of CH_4 during gasification of VW-ST decreased with temperature for both bed materials (exp. 1–5 and 2–6), but more significantly with sand (exp. 1–5). A possible explanation for this dissimilar trend relies on the evolution of tars when temperature increases, which will be discussed in the following section. The results showed an evolution towards lighter tars with increasing temperature when GROT-ST was gasified with sand (de-alkylation and cracking reactions of tar were favoured). However the evolution of tars obtained from VW-ST with sand presented the opposite effect with temperature, i.e. heavier molecular weight distributions. In this case, the tar repolymerization reactions would be predominant, resulting in a decline of CH_4 production. The larger decrease of C_2 concentrations during the experiments with VW-ST under these conditions also supports this hypothesis, as these compounds can be involved in processes of growth of PAH compounds [41,42].

From Fig. 1, it can be observed that the yields of CO and CO_2 increased with increasing temperature and when dolomite replaced sand as bed material. The results for the CO_2 yields by varying temperature evolution can be explained due to higher rates of hydrocarbon oxidation and steam tar reforming with increasing temperature. The increase of CO yield with temperature indicated a more relevant effect of char gasification reactions (Boudouard and water-gas reaction) and the influence of water-gas shift and steam reforming reaction in the studied range of operating conditions [3,4].

CO and CO_2 yields also increased when dolomite was used as bed material, this effect being more significant at lower temperature (750 °C). This increase in the amount of CO and CO_2 produced is related to the higher global gas yield when dolomite was used as material bed, rather than due to an increase on volumetric percentages of these compounds. Comparing the gas composition (vol.%, Table 4), lower levels of CO and CO_2 were obtained for the experiments with dolomite as bed material (exp. 2, 4, 6, and 8) in almost all cases. The effect of water gas-shift reaction (promoted by dolomite) and other reactions involving CO_2, such as dry reforming of tars and light hydrocarbons, would explain these trends.

However, considering the $CO/CO_{2(vol)}$ ratio it can be observed that formation of CO is enhanced at higher temperatures, probably due to higher rates of the Boudouard reaction, and the effect of water gas shift reaction [3,4]. For instance, the $CO/CO_{2(vol)}$ ratio varied from about 0.55 at 750 °C (for both bed materials, exp. 3–4), to 0.66 at 850 °C (exp. 7–8) when GROT-ST was used as feedstock. Regarding the effect of dolomite, the values of $CO/CO_{2(vol)}$ were similar to those obtained with sand as bed material, denoting similar drops, in concentration, for both compounds.

C_2 and C_3 hydrocarbons were produced in lower yields than the rest of the gas species, although their contribution to the calorific value of the producer gas was still significant. Fig. 1 shows a general decrease of C_2 hydrocarbons with temperature, which could be related to the higher rates of cracking and reforming of hydrocarbons at higher temperature together with the fact that these compounds could be involved in the formation of tertiary tar and PAHs, being this process also enhanced at high temperature. The results for the gas compositions from Table 4 show similar dry concentrations of C_2 hydrocarbons at 750 °C for both types of biomass (exp. 1, 2, 3 and 4). However, increasing the gasification temperature to 850 °C led to a large decrease of C_2 when using VW-ST (exp. 1–5 and 2–6) as compared to GROT-ST (exp 3–7 and 4–8), indicating once more the distinct behaviour of the investigated feedstocks. The presence of dolomite also decreased the concentration of C_2 during all the experiments, the relevance of this effect depending on temperature and type of biomass feedstock.

3.3. Tar characterization

This section summarizes the evolution of the tar content in the gasification-product gas, together with a characterization of the produced tar based on its molecular weight distribution, chemical structure, and PAH (polyaromatic hydrocarbon) content.

Table 3
Effect of experimental conditions on product yields.

Exp.	Feedstock	T (°C)	Bed material	Yield (wt.%)		
				Gas	Tar	Char
1	VW-ST	750	Sand	123.2 ± 0.5	0.79 ± 0.01	6.54 ± 0.08
2	VW-ST	750	Dolomite	141.1 ± 0.3	0.39 ± 0.01	7.31 ± 0.10
3	GROT-ST	750	Sand	122.0 ± 0.4	0.81 ± 0.02	6.64 ± 0.08
4	GROT-ST	750	Dolomite	139.5 ± 0.3	0.70 ± 0.03	8.90 ± 0.09
5	VW-ST	850	Sand	142.9 ± 0.2	0.64 ± 0.02	2.28 ± 0.09
6	VW-ST	850	Dolomite	153.0 ± 0.4	0.12 ± 0.02	4.34 ± 0.10
7	GROT-ST	850	Sand	148.1 ± 0.4	0.70 ± 0.02	4.49 ± 0.10
8	GROT-ST	850	Dolomite	151.2 ± 0.2	0.26 ± 0.02	6.21 ± 0.05

Table 4
Effect of temperature and bed material on gas composition. Pressure 0.5 MPa (vol.%), dry and N_2 free.

Feedstock	VW-ST		GROT-ST		VW-ST		GROT-ST	
T (°C)	750	750	750	750	850	850	850	850
Bed material	Sand	Dolomite	Sand	Dolomite	Sand	Dolomite	Sand	Dolomite
Experiment	1	2	3	4	5	6	7	8
H_2	35.91 ± 0.2	36.07 ± 0.3	33.58 ± 0.3	37.93 ± 0.4	38.11 ± 0.3	39.40 ± 0.5	38.08 ± 0.2	39.79 ± 0.4
O_2	0.27 ± 0.02	0.10 ± 0.02	0.01 ± 0.02	0.01 ± 0.02	0.13 ± 0.03	0.10 ± 0.04	0.01 ± 0.02	0.03 ± 0.03
CH_4	7.53 ± 0.05	8.31 ± 0.07	7.46 ± 0.07	7.32 ± 0.04	7.06 ± 0.03	8.09 ± 0.5	7.99 ± 0.04	7.83 ± 0.07
CO	20.67 ± 0.2	22.24 ± 0.1	20.27 ± 0.2	18.56 ± 0.1	21.29 ± 0.1	20.75 ± 0.2	20.92 ± 0.1	20.52 ± 0.2
CO_2	33.88 ± 0.3	31.88 ± 0.2	36.69 ± 0.1	34.61 ± 0.2	32.72 ± 0.2	31.11 ± 0.1	31.81 ± 0.2	31.06 ± 0.3
C_2H_4	1.19 ± 0.02	0.88 ± 0.01	1.33 ± 0.02	1.03 ± 0.02	0.59 ± 0.01	0.46 ± 0.01	0.90 ± 0.01	0.55 ± 0.01
C_2H_6	0.55 ± 0.02	0.51 ± 0.03	0.65 ± 0.02	0.54 ± 0.01	0.09 ± 0.01	0.08 ± 0.03	0.30 ± 0.01	0.21 ± 0.02
C_3H_8	0.00	0.00	0.13 ± 0.02	0.00	0.00	0.00	0.00	0.00

3.3.1. *Tar content*

The variation of tar content in the fuel gas (expressed as g/Nm^3) with temperature and presence of dolomite for both biomasses is shown in Fig. 2. The data show a significant decrease in tar content when dolomite was used as bed material, this effect being more significant at higher temperature. The results from Fig. 2 also show that VW-ST always yielded lower amount of tar in comparison to GROT-ST, under the same experimental conditions. Additionally, the decrease of tar content when using dolomite and increasing temperature was more pronounced for VW-ST as compared to GROT-ST. As an example, the tar content decreased from 2.6 g/Nm^3 at 750 °C to 0.7 g/Nm^3 at 850 °C for VW-ST and dolomite whereas it declined from 4.3 g/Nm^3 to 1.6 g/Nm^3 for GROT-ST and dolomite as bed material.

3.3.2. *Molecular weight distribution (Size exclusion chromatography)*

Fig. 3 shows the molecular weight distributions of tars, which were measured by SEC (size exclusion chromatography). As described in a previous work [33], the chromatograms presented bimodal distributions, with an early eluting peak, or "excluded" peak, and the main peak that corresponds to the material able to penetrate the porosity of the column packing [34]. Molecular weight calibration was performed based on the elution times of PS (polystyrene) standards and PAH (polycyclic aromatic hydrocarbon) standards.

The SEC chromatograms show a clear trend towards lighter tars when dolomite was used as bed material, as compared to sand, for both temperature levels and both types of biomass feedstock. For instance, a comparison of the elution curves (SEC) of tars obtained from GROT-ST at 750 °C with both bed materials (Fig. 3), shows that the maxima at 54.8 (~220 u) in the chromatogram of tars obtained with sand shifted to 56.2 (~180 u) in the presence of dolomite, indicating a clear distribution shift towards lighter MWs when dolomite was used. The lift-off of the retained peak appeared around 40.5 for sand and 42.1 min for dolomite, corresponding to masses of 4950 and 3150 u, respectively.

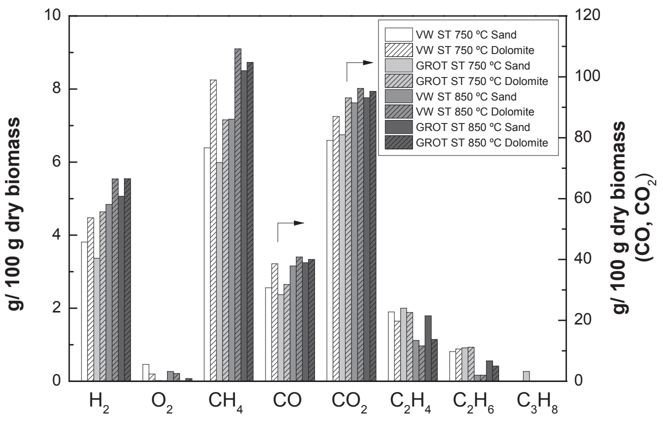

Fig. 1. Effect of temperature and bed material on gas yields. Pressure 0.5 MPa.

The capacity of dolomite to reduce the mean molecular weight of the tars appeared to be more relevant at 850 °C, which can be related to the enhancement of tar cracking reactions as temperature increases. However, the effect of temperature on tar molecular weight distribution when sand was used as bed material depended on the type of biomass feedstock. Tars produced from GROT-ST were lighter as temperature increased, whereas those obtained from VW-ST presented slightly heavier molecular weight when temperature increased. A possible explanation is that the competition between two mechanisms, tar polymerization reactions, and de-alkylation, dehydration and cracking of tars [4,41], differs for the two feedstocks. Cracking reactions would be dominant when dolomite is used as bed material, whereas with sand in the bed, tar repolymerization reactions could be more relevant as temperature increases, competing with cracking reactions. This effect appeared to be influenced by the properties of the biomass and other experimental conditions, as temperature.

3.3.3. *FT-IR analysis*

Figs. 4 and 5 show the influence of bed material and gasification temperature on the functional groups of the tar obtained from the

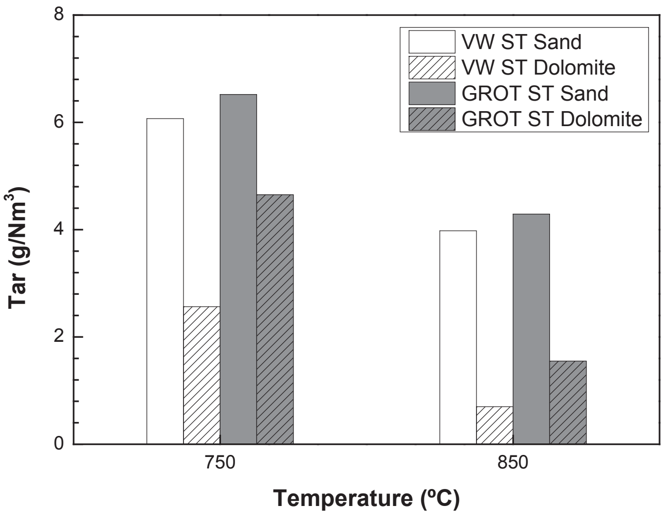

Fig. 2. Effect of temperature and bed material on tar content (GROT vs VW). Pressure 0.5 MPa.

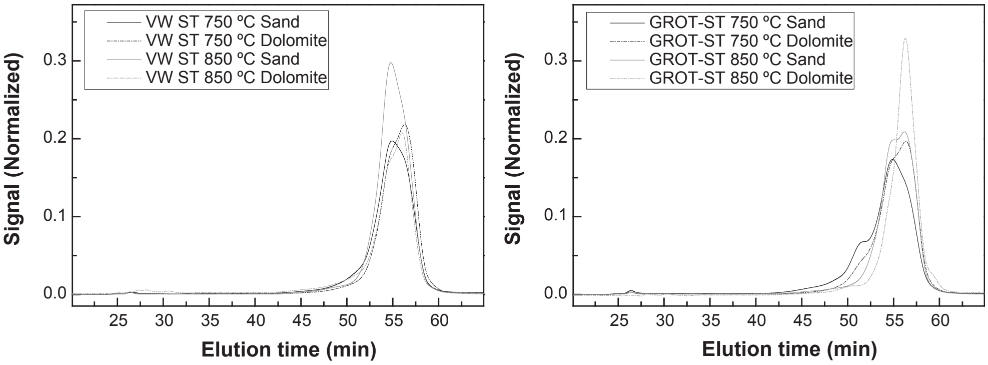

Fig. 3. Size exclusion chromatography analysis of VW-ST and GROT-ST tars obtained in a FBR, influence of temperature and bed material.

gasification of VW-ST and GROT-ST, respectively. The tar FT-IR spectra showed in all cases absorption bands corresponding to aromatic structures at 3050, 1600, 870, 813 and 750 cm^{-1} and aliphatic structures at 2960, 2922, 2855, 1352 and 1379 cm^{-1}. The bands in the region 900–700 cm^{-1} are usually assigned to the out-of-plane bending of aromatic CH groups. The bands in the region 1630–1470 cm^{-1} are assigned to the stretching of aromatic C=C groups and bands at 3050 and 3016 cm^{-1} to the stretching of aromatic C–H groups. The bands in the 2968–2864 and 1444–1377 cm^{-1} regions are due to the stretching and bending modes of saturated aliphatic hydrocarbons (C–H). Additionally, peaks appearing at 1100–1300 and 1700 cm^{-1} are assigned to phenoxyl and ether stretching and carbonyl groups, respectively. In general, for both biomasses and temperatures, tars obtained using dolomite were more aliphatic (aliphatic band: 2990 cm^{-1}) than those obtained with sand. This was more evident when comparing the tars obtained at 850 °C, and less obvious for those at 750 °C and VW-ST as feedstock. Increasing temperature from 750 to 850 °C with sand as bed entailed the production of more aromatic (and less aliphatic tars). However this temperature effect was not evident when dolomite was used in the bed.

The signals corresponding to oxygenated functionalities decreased when temperature increased. Among the oxygen functional groups present in the tars, C=O structures (broad band at 1715 cm^{-1} – 1650 cm^{-1}) and methoxyl groups (1265 cm^{-1}) were detected.

3.3.4. GC–FID analysis

In addition to the previous tar analysis, a detailed characterization of the PAHs (polynuclear aromatic hydrocarbons) presented in the tar samples was carried out. A standard of 16 PAHs (EPA 610 PAH Mix) was used for the identification of the species present in the tar chromatographs. Beside those 16 PAH compounds, three additional compounds (1- and 2-methylnapthalene, and biphenyl) were easily identifiable and included in the list of determined hydrocarbons. In this way, the evolution of these compounds under the different experimental conditions could be tracked. The study was focused on PAHs evolution as these compounds are the main components of tar at the temperature range applied in this study (750–850 °C) [1], together with their relevance as pollutants due to their carcinogenic potential [8]. Two examples of the obtained chromatograms from tars under different conditions (type of biomass and catalyst presence) are shown in Fig. 6.

Fig. 7 shows a comparison between the total amount of PAH compounds and the amount of total tar produced by 100 g of dry biomass. The results show that when dolomite was used as bed material (for both biomasses and temperatures) lower levels of tar were obtained in comparison to those carried out with sand as bed material. The evolution of the amounts of PAH compounds was similar, with only small variations. The main difference appeared when comparing experiments 3 and 4, where a slightly higher level of PAHs was obtained with dolomite as bed material, although the level of total tar was lower. It is worth noting that the relative

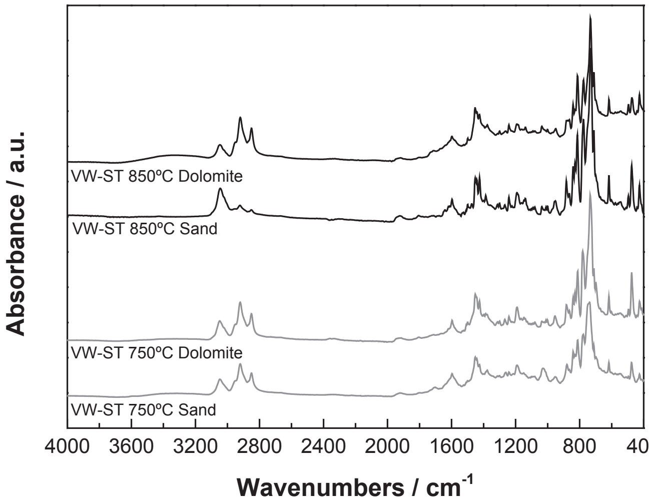

Fig. 4. FTIR spectra of VW-ST tars obtained in a FBR, influence of temperature and bed material.

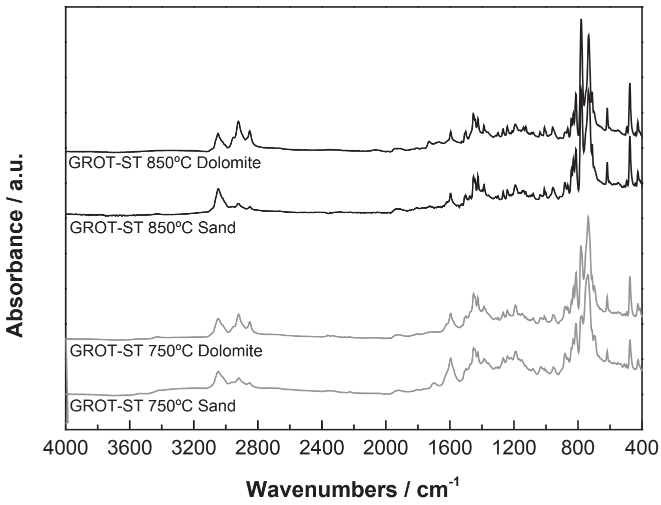

Fig. 5. FTIR spectra of GROT-ST tars obtained in a FBR, influence of temperature and bed material.

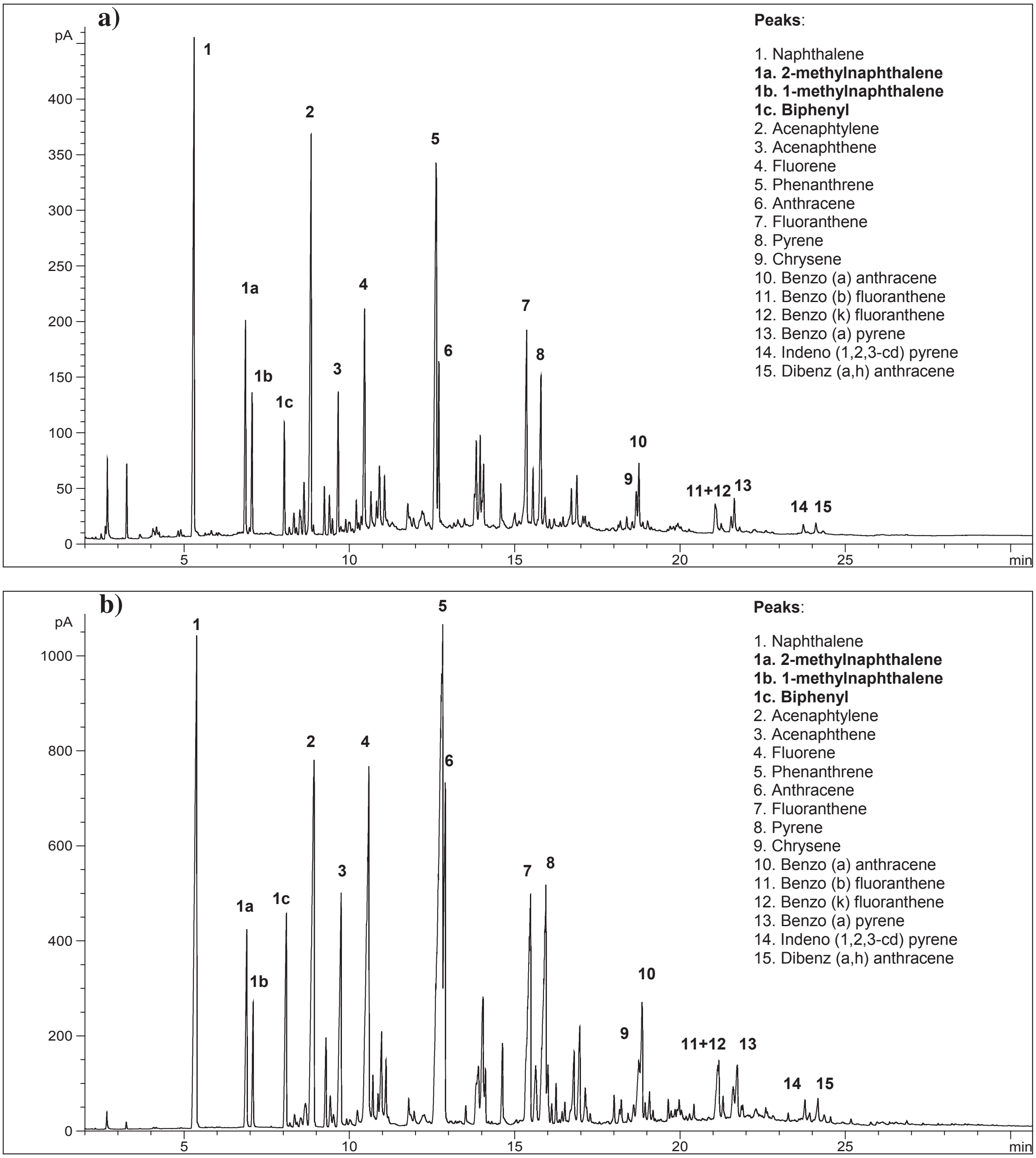

Fig. 6. GC–FID chromatograms of tars obtained in a FBR: a) GROT-ST/750 °C/sand/0.5 MPa, b) VW-ST/dolomite/750 °C/0.5 MPa.

decrease of total tar when using dolomite as bed material was larger than the decrease of PAHs for all the studied conditions. As a result the tars obtained for both feedstocks at 850 °C and dolomite as bed material mainly consisted on PAH compounds (∼84%).

3.3.4.1. Effect of calcined dolomite on PAHs evolution. Figs. 8 and 9 show the yield of the different PAH compounds detected on the tars obtained in the gasification of VW-ST and GROT-ST, respectively. The effect of dolomite on PAHs evolution can be observed comparing even and odd experiments. A decrease in the different tar species was expected due to the use of dolomite in the bed material [22,32]. However the observed effect was different depending on the experimental conditions and feedstock. In the case of experiments 3 and 4 (GROT-ST, 750 °C, Fig. 9) the two main compounds were naphthalene and acenaphtylene. Comparing the total PAH yield for both bed materials, a slight increase in total PAH yield in presence of dolomite was observed. On the other hand, when considering similar conditions but VW-ST as feedstock (Fig. 8), the main PAH compounds were naphthalene, acenaphtylene, phenanthrene and fluoranthene. Additionally, a clear depletion in the yield of all the detected PAH was observed when dolomite was used as bed material (with reductions in the range 31–74%). The most relevant reduction appeared in the case of fluoranthene (with a drop of about 77%), whereas fluorene presented a reduction as little as 3%.

Comparison of experiments 5–6 and 7–8, allowed the evaluation of dolomite effectiveness at 850 °C. Under non-catalytic and

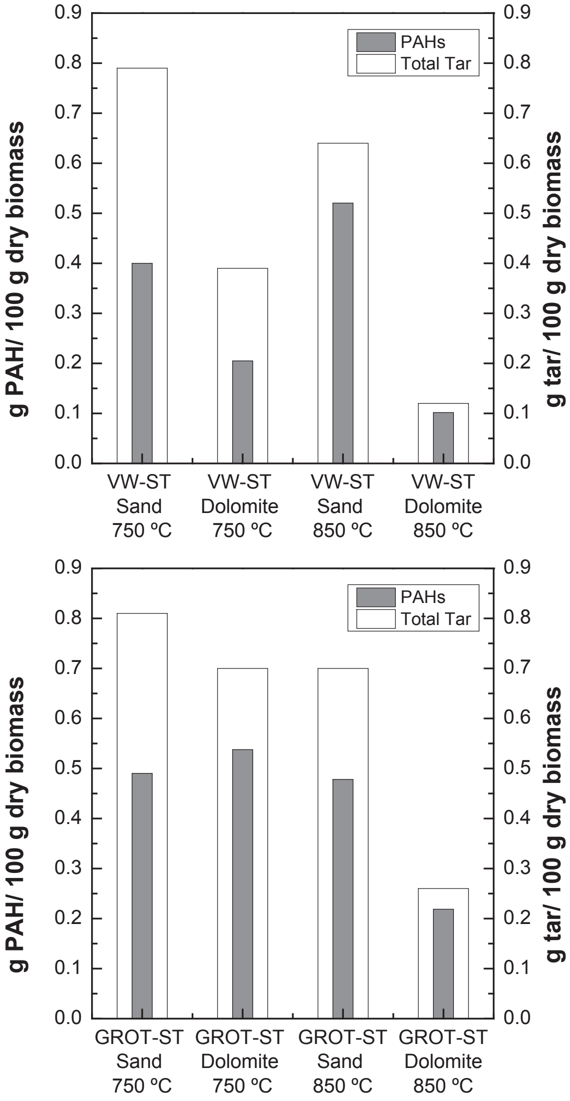

Fig. 7. Effect of temperature and bed material on total tar and PAH yields.

high temperature conditions, the effect of feedstock was less relevant regarding PAH composition. Comparing experiments using both biomasses and sand (exp. 5–7) a similar distribution was observed, being naphthalene, acenapthylene and phenanthrene the major compounds. When dolomite was used as bed material a significant decrease on PAH yields could be observed (exp. 6–8). This drop was even in all the range of PAH compounds for the experiments using VW-ST (exp. 5–6), with reductions in the range 70–90%. On the other hand, in the case of GROT-ST (exp. 7–8), the reduction was more important for heavy PAH (in the order 60–80%), less important for methylnaphthalenes and biphenyl (about 50%), whereas naphthalene presented the lowest reduction with 18%. The observed tar reduction was in concordance with previous works [9,31,32]. Devi et al. [22] studied the catalytic decomposition of biomass tar using calcined dolomite (and untreated olivine) and found that the catalytic conversion of different tar classes increased linearly from 800 to 850 °C. The authors concluded that some compounds, such as naphthalene and acenaphtylene, are very stable compounds (formed due to breakdown of higher tars (GC-undetectable tars and heavy PAH)) and remain in substantial amounts even after severe catalytic treatment up to 900 °C.

3.3.4.2. Effect of temperature on PAHs evolution. The evolution of PAH compounds with temperature presented trends that were dependent on the nature of the bed material (sand vs. dolomite).

A temperature increase from 750 °C to 850 °C, using sand as bed material, led to higher yields of almost all the PAHs considered in the case of VW-ST, and of the most relevant in the case of GROT-ST (naphthalene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benzo anthracene). This is in good agreement with previous studies [4,33], showing an evolution towards heavier PAHs compounds as temperature increases. The reduction observed for some compounds (as methylnaphthalenes and biphenyl) indicates their role as intermediate compounds in the polymerization pathway.

The influence of temperature when dolomite was used could be observed comparing experiments 2–6 and 4–8. In this case the evolution of PAH compounds was opposite to the one observed for sand, with a consistent decrease in the whole range. The only compound that increased in the tar was naphthalene in experiment 8. This fact could be related to the production of this particular compound from the cracking of heavier PAHs [22,43] as higher temperatures provoke an increase in the extent of the thermal cracking reactions: first primary (oxygenated) compounds are destroyed at 400–500 °C, then secondary compounds (phenols and olefins) are further cracked at 500–600 °C, and finally tertiary tar compounds evolve by progressive aromatization at 750–900 °C [8,44]. Considering that the biomass is strongly torrefied and the gasification temperature is above 700 °C, primary tars could be almost inexistent and the maturation of tar is related to secondary-towards-tertiary tars. Moreover, the presence of steam in all experiments also speeds up tar cracking and leads to an increase in tertiary tars through reforming reactions involving all the present hydrocarbons [4].

This study presents some general trends on PAHs evolution, however further work should be taken within this research field for a proper understanding of the inter-relation among different tars and their kinetics. The results here discussed confirmed the trends observed recently in a previous work [33] showing that high temperatures and pressures favour PAHs polymerization when using sand as bed material. The effect of dolomite as bed material under the same temperature conditions was positive in this regard, leading to lower tar content in the flue gas.

4. Conclusions

The increase in temperature (from 750 °C to 850 °C) and the presence of calcined dolomite on the bed material proved to be beneficial in the gasification of torrefied biomasses (VW-ST and GROT-ST), not only to enhance gas yields but also to reduce tar formation.

The effect of the experimental conditions (temperature, feedstock type and presence of catalyst) on gas composition has been evaluated taking into account the main gasification reactions (water-gas, Boudouard, methanation, steam reforming and water gas-shift), and their relation with the evolution of tar and char fractions.

The catalytic effect of dolomite promoted tar cracking towards gas products and thus higher gas yield. Similar results were obtained for both biomasses at 750 °C although a higher production of gas was detected at 850 °C. Regarding the gas composition, tar destruction reactions promoted by the catalyst (dolomite) shifted to higher content of some components (H_2, CO_2, CO and CH_4) whereas C_2 hydrocarbons decreased, an effect that was slightly more relevant at 850° C. Comparable trends were observed with increasing temperature, which had a positive effect on cracking reactions and tar destruction. For both feedstocks, the increase in

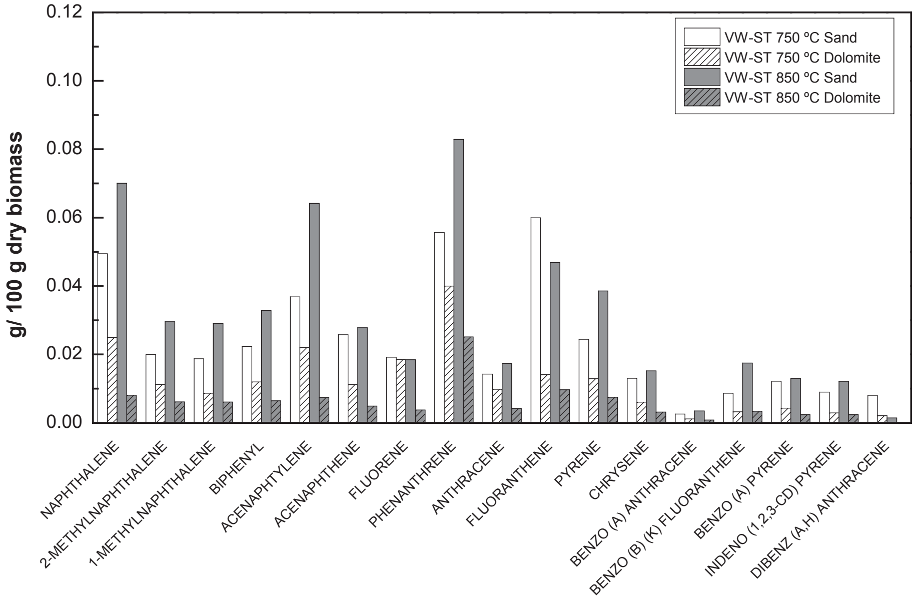

Fig. 8. Effect of temperature and bed material on tar composition (VW-ST).

temperature resulted in (i) higher gas yields (H_2, CH_4, CO and CO_2), and (ii) enhanced char gasification reactions (with steam). On the other hand, C_2 hydrocarbons were present in lower concentration especially at 850 °C.

The evolution of tar yields and tar composition revealed a possible competition between two reaction pathways involving tars during the gasification process: (i) tar polymerization reactions, and (ii) de-alkylation, dehydration and cracking of tars. Cracking reactions would be dominant when dolomite is used as bed material, whereas with sand in the bed, tar repolymerization reactions could be more relevant as temperature increases, competing with cracking reactions. This effect, also supported by the evolution of char yield, appeared to be influenced by the properties of the biomass and other experimental conditions, as temperature.

It is worth noting that tars from both biomasses presented some differences regarding composition, although in all cases the three major compounds were naphthalene, acenapthylene and phenanthrene.

The study revealed VW-ST as a potentially better feedstock for biofuels and CHP systems as compared to GROT-ST, with slightly greater gas yield, and lower tar and char formation. The use of dolomite and temperature increase also resulted in enhancing the gasification process.

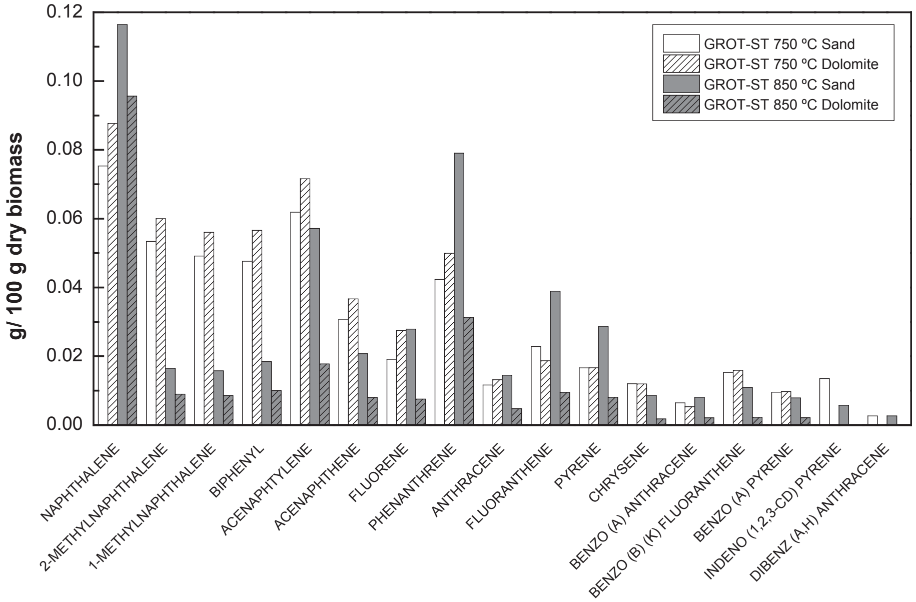

Fig. 9. Effect of temperature and bed material on tar composition (GROT-ST).

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